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DERWENT-WEEK: 200111

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TITLE: Process for  
the manufacture of fatty acid  
esters from  
                          ricin oil and  
                          mono-alcohols uses a heterogeneous  
                          catalyst  
                          based on zinc  
and aluminum with a spinel  
structure in a

transesterification reaction and  
separation

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PATENT-ASSIGNEE: INST FRANCAIS DU  
PETROLE [INSF]

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PATENT-FAMILY:

PUB-NO	PUB-DATE
LANGUAGE	
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15, 2000	FR

APPLICATION-DATA:

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descriptor	APPL-NO
APPL-DATE	
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1999FR-007520	June 11, 1999

INT-CL-CURRENT:

TYPE	IPC	DATE
CIPS	C07C67/03	20060101

ABSTRACTED-PUB-NO: FR [REDACTED] A1

BASIC-ABSTRACT:

NOVELTY - The use of the zinc/aluminum oxide catalyst enables the production of pure esters and glycerin by a

process which involves few stages and results in products of high purity.

DESCRIPTION - Process for the manufacture of a fatty acid ester and glycerin to a high state of purity by the reaction of a ricin oil with a 1 - 18C aliphatic mono-alcohol .The reaction is effected in the presence of a catalyst chosen from zinc oxide, a mixture of zinc oxide and alumina or a zinc aluminate consistent with the formula :  $ZnAl_2O_4$ ,  $xZnO$ ,  $yAl_2O_3$  ( $x$ ,  $y = 0 - 2$ ).

INDEPENDENT CLAIMS are also included for the ester compositions obtained and the glycerin.

USE - Methyl esters obtained can be used as fuels and the ethyl, isopropyl and

butyl esters have possible uses as lubricants.

ADVANTAGE - The ricin oil has a very specific composition and contains about

90% of 12-hydroxy-9-octadecenoic acid. The catalyst used in the invention

inhibits the dehydration of the acid to the conjugated diene, 9,11, compound.

The reaction produces a secondary product, glycerin, which is obtained in a pure form.

#### EQUIVALENT-ABSTRACTS:

#### ORGANIC CHEMISTRY

The mono-alcohol is preferably a 1 - 5C compound. The catalyst is preferably a zinc aluminate, and the process is operated at 150 - 250degreesC. (more preferably 170 - 200degreesC.) and at a pressure lower than 100 bars.

The mono-alcohol is in excess relative to the stoichiometry alcohol / oil. The zinc aluminate catalyst is in the form of powder, extrudates or balls, and has a surface area of 10 - 200 m<sup>2</sup>/g (more preferably 50 - 200 m<sup>2</sup>/g), a porous vol. of 0.2 - 1.2 cm<sup>3</sup>/g (more preferably greater than 0.3 cm<sup>3</sup>/g) and a pore distribution between 0.01 - 0.1 micro. The reaction may be carried out in discontinuous or continuous modes. In the continuous process, the reaction is effected in fixed beds or in autoclaves and separators in series. For a reaction carried out in fixed beds the VVH is between 1 / 1 to 3 / 1. The preferred process involves the following stages :

- (a) an initial transesterification

with a conversion of oil to ester of at least 80 - 85% ;

(b) evaporation of the excess alcohol ;

(c) separation of the glycerin and the ester, the latter being recycled in a second stage to another transesterification with part of the mono-alcohol recovered in the first evaporation ; and

(d) another evaporation of the mono-alcohol and cold separation of the glycerin and ester.

A pre-stage operation is necessary if the initial ricin oil contains a fatty oil, to effect a glycerolysis of the free fatty acid with a suitable transesterification catalyst, at 180 - 220 degrees C. and 1 bar or

less. The glycerin is separated from the ester by water washing or preferably by the use of specific adsorbents, such as an ion exchange resin. The ester may be subsequently purified by passing over a resin, earth and/or active carbon.

Methyl esters may be prepared by the use of methanol, and ethyl esters using ethanol mixed with 1 - 50% of methanol. The glycerin obtained may be purified by passing over a resin, earth and/or active carbon. The ester compositions obtained have a sterol ester content of less than 0.2% and a mono- and di-glyceride content of 0.5 - 3%, almost total absence of triglycerides and total absence of conjugated dienes which could result from the dehydration

reaction of the ricinoleic acid chain. The glycerin obtained in the process has a purity greater than 99.5%.

120 g of a refined ricin oil was placed in a 500 cm<sup>3</sup> stirred autoclave together with 120 g of dry methanol and 1.2 g of zinc aluminate previously calcined at 700degreesC. The mixture was heated to 210 - 220degreesC., the pressure rising to 40 bar. Samples were taken after 2 hs and 6 hs, the conversion being 89% and 92.7% respectively. Analysis of the ester fraction by GLC did not detect the presence of a 9,11 conjugated methyl acid ester, indicating no dehydration. The same recycled catalyst gave, after 2 hs and 6 hs in the same conditions, conversions of 90.15 and 93.3%. A comparative trial was carried out,

without a catalyst, using 150 g of ricin oil and 150 g of methanol heating for 6 hs at

220degreesC. The partial pressure of methanol attained 40 bars at 200degreesC., and stabilized at 30 bars after 5 hs of reaction.

Analysis by

GLC at the end of the trial gave : -79.7% of methyl esters ; 2.3% of triglycerides ; 6.3% of diglycerides ; and 11.75 of monoglycerides.

Determination of water content of the reaction mixture before and after

reaction gave values of 925 ppm and 1725 ppm respectively. This was equivalent

to a degree of dehydration of the ricinoleic acid ester molecule of 2.3%. GLC

analysis showed the presence of 2.2% of the 9,11 conjugated linolenic acid

confirming dehydration of the ricinoleic acid.

TITLE-TERMS: PROCESS MANUFACTURE  
FATTY ACID RICIN OIL MONO  
HETEROGENEOUS

CATALYST BASED ZINC  
SPINEL STRUCTURE  
TRANSESTERIFICATION REACT  
SEPARATE

DERWENT-CLASS: D23 E17 H07

CPI-CODES: D10-A01; E10-G02D; E10-  
G02E; H07-A; N01-C; N03-F;

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

H4 H401 H481 H7 H721 H8  
J0 J011 J2 J271  
M210 M211 M272 M281 M316 M321  
M331 M342 M381 M391  
M416 M720 N104 N442 N513 N514  
N521 N522 N523 Q271

Q416

Specific Compounds

RA36GZ

Registry Numbers

353919

Chemical Indexing M3 \*02\*

Fragmentation Code

H4 H401 H481 H7 H721 H8

J0 J011 J2 J271

M210 M212 M272 M281 M316 M321

M331 M342 M381 M391

M416 M720 N104 N442 N513 N514

N521 N522 N523 Q271

Q416

Specific Compounds

RA36H0

Registry Numbers

353920

Chemical Indexing M3 \*03\*

Fragmentation Code

H4 H401 H481 H7 H721 H8

J0 J011 J2 J271

M210 M213 M232 M272 M281 M316

M321 M331 M342 M381

M391 M416 M720 N104 N442 N513

N514 N521 N522 N523

Q271 Q416

Specific Compounds

RA36H1

Registry Numbers

353921

Chemical Indexing M3 \*04\*

Fragmentation Code

H4 H401 H481 H7 H721 H8

J0 J011 J2 J271

M210 M214 M231 M272 M281 M316

M321 M331 M342 M381

M391 M416 M720 N104 N442 N513

N514 N521 N522 N523

Q271 Q416

Specific Compounds

RA36H2

Registry Numbers

353922

Chemical Indexing M3 \*05\*

Fragmentation Code

H4 H401 H481 H7 H721 H8

J0 J011 J2 J271

M210 M211 M212 M213 M214 M215

M216 M220 M221 M222

M223 M224 M225 M226 M231 M232

M233 M272 M281 M316

M321 M331 M332 M333 M340 M342

M349 M381 M391 M416

M720 N104 N442 N513 N514 N521

N522 N523 Q271 Q416

Markush Compounds

003178701

Chemical Indexing M3 \*06\*  
Fragmentation Code  
H4 H401 H481 H8 M210 M211  
M272 M281 M320 M416  
M620 M730  
Specific Compounds  
R00270  
Registry Numbers  
15

Chemical Indexing M3 \*07\*  
Fragmentation Code  
M730  
Specific Compounds  
RA17PU  
Registry Numbers  
114651

Chemical Indexing M3 \*08\*  
Fragmentation Code  
H4 H401 H481 H7 H721 H8  
J0 J011 J1 J171  
M280 M316 M321 M331 M342 M381  
M391 M416 M730  
Specific Compounds  
R06482 R14559

Registry Numbers  
105647

Chemical Indexing M3 \*09\*  
Fragmentation Code  
A430 A940 C108 C550 C730 C801  
C802 C803 C804 C805  
C807 M411 M730 Q421  
Specific Compounds  
R01520  
Registry Numbers  
866

Chemical Indexing M3 \*10\*  
Fragmentation Code  
A313 A430 A940 A980 C108 C730  
C801 C802 C803 C804  
C805 C807 M411 M730 Q421  
Specific Compounds  
R07696  
Registry Numbers  
130915

UNLINKED-DERWENT-REGISTRY-NUMBERS:  
0270U; 0270S ; 1520U ; 1520S

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